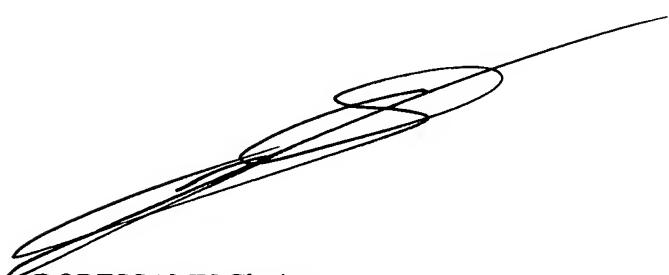


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CERTIFICATION OF TRANSLATION

I, Clarisse DORESSAMY, of CABINET PLASSERAUD, 65/67 rue de la victoire, 75440 PARIS CEDEX 09, FRANCE, do hereby declare that I am well acquainted with the French and English languages, and attest that the document attached is a true English language translation of the text of International Patent Application no.FR 03/01818.

Dated this 2nd of December, 2004

A handwritten signature in black ink, appearing to read "DORESSAMY Clarisse".

DORESSAMY Clarisse

LITHIUM CELL BATTERY

The invention relates to a lithium electrochemical cell battery comprising at least one positive electrode (or cathode), at least one liquid electrolyte comprising at least one lithium salt, and at least one negative electrode (or anode). The invention also relates to the process for manufacturing such a battery and to the use thereof.

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The extraordinary growth of the market for portable electronic equipment has generated, upstream, greater and greater competitiveness in the field of rechargeable batteries or cells. Apart from mobile telephones, which have undergone extremely rapid development, the sales of portable computers, growing at 20% per year, entail new requirements as regards the performance of their power supplies. To this should also be added the expansion of the market for camcorders, digital cameras, portable CD players, wireless devices and numerous toys that more and more often require rechargeable batteries. Finally, it is probable that the 21st century will experience a considerable growth in electric vehicles, the emergence of which will result from the increasingly strict international regulations as regards toxic emissions by internal combustion engines.

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Although the battery market is presently a very attractive one, it is however important to make the right choice so as to be able to position ourselves for the new generation of electronic devices. In fact, it is the progress made in electronics that dictates the specification for tomorrow's batteries. Added to the demand for more self-sufficient batteries has, in recent years, owing to miniaturization, the desire to have thinner and more flexible batteries. Dry polymer technology and Li-ion polymer technology may provide

this flexibility. However, the first technology can operate only at temperatures above 60°C and therefore is inappropriate for portable applications. As regard the second technology, this is currently penetrating
5 the portable market at the expense, at the very least, of a loss of energy associated with the use of carbon rather than lithium.

Lithium ion batteries use gelled high-strength
10 membranes based on fluoropolymers, for example PVDF (polyvinylidene fluoride), which are however, incompatible with Li metal (dimerization reaction at the interface). However, in addition to dendrite problems, other technological barriers regarding the
15 compatibility of the polymers with Li metal remain to be raised. Specifically, dry polymer technology uses PEO (polyethylene oxide) and the gelling of this polymer, although possible, results in a membrane that adheres well to Li but is of low mechanical strength
20 and consequently not easy to manufacture. To alleviate these difficulties, it has been envisaged to blend together two polymers, PEO and PVDF-HFP ((polyvinylidene fluoride)-co-(hexafluoropropylene)) so as to combine adhesion and mechanical strength
25 properties. Thus, patent US-A-6 165 645 describes a gelled electrolyte for a lithium polymer battery, which comprises a polymer alloy and an organic electrolyte solution. Such an alloy comprises a polymer that is difficult to dissolve in the electrolyte solution, for
30 example PVDF, and another polymer that is soluble in said solution, for example PEO. However, the battery using the technology as described in patent US-A-6 165 645 suffers from cyclability problems associated with the formation of lithium dendrites.

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The inventors have found that, thanks to the battery according to the invention, it is possible to optimize the use of a layer of plasticized separator, called PS, comprising at least one plasticizable polymer, called

PP, slightly solvated by the liquid electrolyte, and of a layer of a gelled separator, called GS, comprising at least one gellable polymer, called GP, which is predominantly gelled by the liquid electrolyte.

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- According to the invention, the term "plasticizable polymer" is understood to mean a polymer which can be plasticized by contacting it with the liquid electrolyte, that is to say it has a low affinity for the liquid electrolyte. According to the invention, the term "plasticized separator layer" is understood to mean a layer of a separator comprising predominantly at least one plasticized polymer. Such a layer is generally such that the mechanical strength of the layer of plasticizable polymer is maintained after being contacted with the liquid electrolyte, that is to say after the layer of plasticized polymer has been formed.
- 10 15 20 25 30
- According to the invention, the term "gellable polymer" is understood to mean a polymer which can be gelled by contacting it with the liquid electrolyte, that is to say which has a high affinity for the liquid electrolyte. According to the invention, the term "layer of gelled separator" is understood to mean a layer of a separator comprising predominantly at least one gelled polymer. Such a layer is in general such that the mechanical strength of the layer of gellable polymer is lost after coming into contact with the liquid electrolyte, that is to say after the gel, namely the gelled polymer, has been formed.

The battery according to the invention is a lithium electrochemical cell battery comprising at least one positive electrode (or cathode), at least one liquid electrolyte comprising at least one lithium salt, and at least one negative electrode (or anode), said battery being characterized in that it comprises at least one layer of a gelled separator GS comprising at

least one polymer GP, able to be gelled by the liquid electrolyte, which is at least partly, preferably almost completely gelled by the liquid electrolyte, in contact with the negative electrode, and in that it
5 includes at least one layer of a plasticized separator PS comprising at least one polymer PP, able to be plasticized by the liquid electrolyte, which is at least partly, preferably almost completely, plasticized by the liquid electrolyte and at least partly,
10 preferably almost completely, in contact with the layer of separator GS.

The battery according to the invention thus comprises at least one alternation of a positive electrode, a
15 separator and a negative electrode, or cell. According to the invention, the battery may comprise several of these alternations or cells.

Advantageously, the contact between the negative
20 electrode and the separator GS layer ensures adhesion, thanks to the physical properties of the "glue" which the polymer GP gelled by the liquid electrolyte forms, and also ensures a high-quality interface. In addition, the presence of the polymer PP ensures mechanical
25 strength of the separator PS. According to the invention, the term "separator" is understood to mean a physical means for separating the two electrodes, that is to say a physical means that prevents any contact between the negative electrode and the positive
30 electrode, while still allowing the ionic species necessary for the operation of the battery to pass through it.

According to one embodiment of the invention, the
35 separator PS layer is at least partly, preferably almost completely, in contact with the positive electrode. In such a case, the separator is referred to as a bilayer separator. Thus, in this case, said battery preferably comprises, from the positive

electrode to the negative electrode, a double layer consisting of a separator PS layer and a Separator GS layer.

- 5 According to another embodiment of the invention, battery comprises, in addition, another separator GS layer, called GS_a, at least partly, and preferably almost completely, between the positive electrode and the separator PS layer. To simplify matters, when
10 reference is made in the rest of the text to the properties or the nature of the Separator GS layer, the same also applies of course to the separator GS_a layer. In such a case, the separator is referred to as a three-layer separator. Thus, in this case, said battery
15 preferably comprises, from the positive electrode to the negative electrode, a triple layer consisting of a GS_a separator layer, a separator PS layer and a separator GS layer.
- 20 The polymer PP is chosen from the group formed by polyvinylidene fluoride PVDF, polystyrene PS, polyvinyl chloride PVC, polycarbonate PC, ethylene-propylene-diene monomer EPDM, and derivatives thereof. The term "derivatives" is understood to mean any crosslinked
25 polymer or copolymer obtained from one of these polymers. Preferably, the polymer PP is chosen from a group formed by polyvinylidene fluoride PVDF and (polyvinylidene fluoride)-co-(hexafluoropropylene) PVDF-HFP copolymers generally comprising from 0
30 (exclusive) to 30 mol%, preferably from 4 to 12 mol%, of HFP. Even more preferably, the polymer PP is PVDF-HFP copolymer generally comprising from 0 (exclusive) to 30 mol%, preferably from 4 to 12 mol%.
- 35 The polymer GP is generally chosen from the group formed by polymethyl methacrylate PMMA, polyethylene oxide PEO and polyacrylonitrile PAN, and derivatives thereof such as, for example, crosslinked polyethylene oxide copolymers generally comprising at least one unit

chosen from the group formed by epichlorhydrin units, propylene oxide units and allyl glycidyl ether units. Preferably, the polymer GP is PEO.

5 The positive electrode preferably comprises carbon, active material, polymer PP and optionally at least one plasticizer. The term "plasticizer" is understood to mean an organic liquid or an oligomer having a low affinity for a polymer PP. Such a plasticizer thus
10 makes it possible to create, within the polymer PP, pores that the plasticizer had occupied. Preferably, such pores may be freed by passing the material through a bath of a nonsolvent for the polymer PP, or by any other method known to those skilled in the art for
15 extracting plasticizer without modifying the structure of the polymer PP. Advantageously, during the operation of the lithium battery, such pores are occupied by liquid electrolyte, which participates in the electrochemical reactions at the positive electrode.

20 More generally, the positive electrode may comprise at least one transition metal oxide (a transition metal being an element of one of the groups of the Periodic Table of the Elements) capable of reversibly inserting
25 and extracting lithium, for example an oxide chosen from the group formed by LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiV_3O_8 , V_2O_5 , V_6O_{13} , LiFePO_4 and Li_xMnO_2 ($0 < x < 0.5$). In general, the positive electrode also includes a current collector, for example made of aluminum.

30 The negative electrode is preferably based on lithium metal, that is to say it mainly comprises lithium metal. However, more generally, the negative electrode may comprise metallic lithium, a lithium alloy and
35 carbon or an inorganic compound capable of reversibly inserting and extracting lithium. The negative electrode may also include a current collector, for example made of copper.

The liquid electrolyte generally comprises at least one lithium salt such as, for example, the salts chosen from the group formed by LiCF₃SO₃, LiClO₄, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂, LiAsF₆, LiPF₆, and LiBF₄.

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The plasticizer optionally present is generally chosen from the group formed by PEO oligomers, dibutyl phthalate (DBP) and propylene carbonate (PC).

10 The invention also relates to a process for manufacturing a lithium electrochemical cell battery comprising at least one positive electrode (or cathode), at least one liquid electrolyte comprising at least one lithium salt, and at least one negative electrode (or anode) comprising an assembly of at least one layer of gelled separator GS, comprising at least one polymer GP, able to be gelled by the liquid electrolyte, on the negative electrode, of at least one layer of plasticized separator PS, comprising at least one polymer PP, able to be plasticized by the liquid electrolyte, on said separator GS layer, and optionally of at least one other layer of gelled separator GS, called GS_a, comprising at least one polymer GP, on said separator PS layer, the combination of these two or 25 three layers constituting a separator between the negative electrode and the positive electrode, an assembly of said separator on the positive electrode, and an impregnation of said separator by the liquid electrolyte.

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In one method of implementing the process according to the invention, the positive electrode is generally manufactured in solution from polymer PP, carbon, active material, plasticizer and solvent.

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In another method of implementing the process according to the invention, the positive electrode is generally manufactured by extrusion from polymer PP, carbon, active material and plasticizer.

In another method of implementing the process according to the invention, the separator PS layer is generally manufactured in solution from polymer PP, plasticizer and solvent.

In another method of implementing the process according to the invention, the separator PS layer is generally manufactured by extrusion from polymer PP, plasticizer or liquid electrolyte.

In another method of implementing the process according to the invention, the separator GS layer is generally manufactured in solution from polymer GP, solvent and optionally plasticizer.

In another method of implementing the process according to the invention, the separator GS layer is generally manufactured by extrusion from polymer GP, solvent and optionally plasticizer or liquid electrolyte.

Preferably, the polymer PP is generally filled with at least one mineral compound chosen, for example, from the group formed by MgO, SiO₂, Al₂O₃, TiO₂, BaTiO₃ and lithium salts such as LiAlO₂ and LiI.

Preferably, the polymer GP is generally filled with at least one mineral compound chosen, for example, from the group formed by MgO, SiO₂, Al₂O₃, TiO₂, BaTiO₃ and lithium salts such as LiAlO₂ and LiI.

In one method of implementation, the two or three PS and GS layers are joined together into a separator by hot lamination or hot calendering. The term "lamination" is understood to mean passing the layers between two rolls, the gap between which is kept constant. The term "calendering" is understood to mean passing the layers between two rolls, the pressure applied by the two rolls being constant. The expression

"hot lamination or hot calendering" is understood to mean an operation carried out at a temperature generally between 50 and 140°C for example about 130°C. The pressure exerted by the rolls is generally between 5 about 5 psi and about 30 psi, that is to say between about 0.035 MPa and about 0.21 MPa, for example about 20 psi (i.e. about 0.14 MPa).

In another method of preparation, said layers form a 10 three-layer separator obtained by passing the separator PS layer into a solution of polymer GP, or into a solution of liquid electrolyte in which the polymer GP has been dissolved.

15 In another method of preparation, said layers form a bilayer separator obtained by passing a separator PS layer, preassembled with the positive electrode, into a solution of polymer GP or into a solution of liquid electrolyte in which the polymer GP has been dissolved.

20 The positive electrode and the separator are generally joined together by hot lamination or hot calendering in order to form a plastic complex.

25 In addition, the plasticizer(s) optionally present in the positive electrode separator assembly is (are) removed by washing or vacuum extraction so as to obtain an assembly containing virtually no plasticizer.

30 The separator/positive electrode assembly, preferably containing virtually no plasticizer, is generally brought into contact with the negative electrode by a lamination or calendering step optionally carried out hot.

35 The polymer PP, the polymer GP, the positive electrode, the negative electrode, the liquid electrolyte and the plasticizer are, within the context of the process according to the invention, generally chosen in the

same way as explained above in the case of the battery according to the invention.

Finally, the invention relates to the use of a battery
5 as described above or manufactured according to the process as described above for a hybrid vehicle, an electric vehicle, for a stationary application (i.e. emergency power supply provided by a battery in the case of a breakdown of the electrical mains) or
10 portable equipment application.

The invention will be more clearly understood and other features and advantages will become apparent on reading the following description, which is given by way of
15 nonlimiting example and with reference to figures 1 to 7.

Figure 1 shows a schematic cross section through a battery having a bilayer separator according to the
20 invention.

Figure 2 shows a schematic cross section through a comparative battery according to the prior art.

25 Figure 3 shows the percentage recovered capacity (C in %) as a function of the number of cycles (N) for the battery according to the invention of figure 1 and for the battery according to the prior art of figure 2, under slow cycling.

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Figure 4 shows the percentage recovered capacity (C in %) as a function of the number of cycles (N) for the battery according to the invention of figure 1, under rapid cycling.

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Figure 5 shows a schematic cross section through a battery according to the invention.

Figure 6 shows the percentage recovered capacity (C in

%) as a function of the number of cycles (N) for a battery according to the invention of figure 5.

Figure 7 shows a schematic cross section through a 5 battery having a three-layer separator according to the invention.

Figure 1 shows a schematic cross section through a 10 battery 10 having a bilayer separator (3, 4) according to the invention. The battery 10 comprises the negative electrode collector 1, for example made of copper, a negative electrode 2 (the active part) which is, for example, a layer of Li metal, a layer 3 consisting for 15 example of a PEO layer, a layer 4 consisting for example of a layer of PVDF-HFP containing 12 mol% HFP, a layer 5 (the active part of the positive electrode) and a positive electrode current collector 6, for example made of aluminum. The presence of the collector 1 is not essential - this is why collector 1 has been 20 shown in dotted lines.

Figure 2 shows a schematic section through a comparative battery 11 according to the prior art, which comprises all the elements of figure 1 in the 25 case when a connector 1 is present, except for the layer 3.

Figure 3 will be commented upon below in Example 1.

30 Figure 4 will be commented upon below in Example 2.

Figure 5 is a schematic cross section through a battery 12 having a bilayer separator (13, 14) according to the invention, which comprises all the elements of figure 1 35 with the exception of the layer 3. Instead of the layer 3 there is a layer 13 that consists, for example, of a PEO gel layer, spread for example with a brush over the layer 4 during manufacture of the battery 12.

Figure 6 will be commented upon below in Example 4.

Figure 7 shows a schematic cross section through a battery 14 having a three-layer separator (3, 4, 15) 5 according to the invention, the battery 14 comprises all the elements of figure 1, to which has been added a later 15, for example made of PEO, between the layer 4 and the layer 5.

10

EXAMPLES

The examples below illustrate the invention without in any way limiting its scope.

15 Process for manufacturing the battery according to the invention of Examples 1 and 2

The manufacturing process described below relates to the manufacture of a single-cell battery 10, that is to say a battery consisting of a single succession of a negative electrode (5, 6), a positive electrode (1, 2) and a bilayer separator (3, 4) consisting of a layer 3 of polymer GP, which is for example PEO gelled by liquid electrolyte, and of a layer 4 of plasticized polymer, which is for example PVDF-HFP, the layer 3 being placed between the negative electrode (1, 2) and the layer 4, and the layer 4 being placed between the positive electrode (5, 6) and the layer 3. In the case described in Examples 1 to 4, the negative electrode (1, 2) comprises lithium metal 2, optionally with a copper collector 1. The positive electrode (5, 6) comprises an aluminum current collector 6 and a layer 5 of active material.

35 The PEO layer 3 is manufactured from a PEO/acetonitrile mixture, the acetonitrile being left to evaporate for several hours on a glass plate or on a sheet of Mylar®. Typically it has a thickness of 15 µm. The PVDF-HFP layer 4 is obtained using a technology that consists in

spreading, onto a Mylar® support, using a device of the doctor-blade type, a solution comprising PVDF-HFP, DBP (dibutyl phthalate), SiO₂ and acetone. A plastic layer for the positive electrode is obtained by spreading a
5 solution comprising PVDF-HFP, DBP, active material (LiV₃O₈) and carbon in weight ratio of 10:1. Assembly of the cell comprises firstly thermal bonding of the plastic positive electrode 5 to the aluminum current collector 6 by hot calendering at a temperature close
10 to 135°C and at a pressure of about 20 psi (i.e. about 0.14 MPa). The resulting assembly is then bonded hot lamination, at a temperature close to 130°C and at a pressure of about 20 psi (i.e. about 0.14 MPa), to the two layers 3 and 4 of the bilayer separator (3, 4)
15 (PVDF-HFP, PEO). The DBP is then extracted by passing the assembly through an ether bath in order to obtain a porous membrane. This porous membrane is then dried and placed inside a glove box of the Jacomex type, for example a Jacomex BS531NMT4 glove box, guaranteeing a
20 moisture content of less 1 ppm, filled with an inert gas (argon) in order for the material once again to be imbibed with a liquid electrolyte. This liquid electrolyte fills the pores left vacant by the plasticizer and gels the PEO. Finally, the membrane (3,
25 4, 5, 6) thus obtained is deposited on the Li metal negative electrode 2 hot-laminated beforehand onto a copper grid 1 as current collector. It is important to note that the Li/electrolyte interface is formed *in situ* via the formation of a gel during the contacting
30 of the PEO layer with the liquid electrolyte. The assembly is then hermetically sealed in an aluminum-lined plastic bag (of the "Blue Bag" type from Shield Pack) for electrochemical testing.

35 It may be noted that the PVDF-HSP/PEO separator (3, 4) can also be manufactured according to the invention in another way, namely:

- passing the PVDF-HFP membrane through a PEO acetonitrile solution so as to leave a thin film on the

surface or covering the membrane, for example using a brush, with said thin film (see Example 3);

- passing the PVDF-HFP membrane through a liquid electrolyte in which a certain quantity of PEO has already been dissolved (see Example 4).

Example 1: Slow cycling of a battery

A battery comprising an LiV_3O_8 -based positive electrode (5, 6), a PVDF-HFP/PEO separator (3, 4), consisting of two layers 3 and 4, and a lithium metal negative electrode (1, 2), mounted under the conditions described above, was galvanostatically cycled between 3.5 and 2 volts at a rate equivalent to the insertion of one lithium ion in 5 hours. The liquid electrolyte used was a mixture of ethylene carbonate and propylene carbonate, in a 1:1 mass ratio, and of a lithium salt known as LiTFSI (lithium trifluoromethanesulfonimide) (in fact the salt $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ sold under the brand name FLUORAD™ HQ-115 by 3M) in a concentration of 1 mol per liter of solvent. Figure 3 shows the percentage recovered capacity (C in %) as a function of the number of cycles (N), indicated by curves 7 and 8. Curve 7 is the curve obtained with a battery 10 according to the invention, as shown schematically in Figure 1. Curve 8 is the curve obtained with a comparative battery 11, as shown schematically in figure 2. Comparison between the two curves 7 and 8 shows that the insertion of a gelled PEO layer between the lithium metal anode and the PVDF/HFP-based separator, allows a battery to undergo more than 120 cycles, while maintaining a capacity of more than 80% of its initial capacity (the end-of-life criterion for industrial batteries).

35 Example 2: Rapid cycling of a battery according to Example 1

To approach the industrial requirements in terms of cycling rate, the battery 10 shown in figure 1

underwent the following electrochemical test program:

- a first cycle comprising a discharge at -0.2 mAh/cm^2 and a charge at 0.1 mAh/cm^2
- the other cycles comprise a discharge of the battery in 2 hours (C/2) and a charge in 10 hours (C/10).

In both cases, the limiting voltages were 3.3 V and 2 V.

10 Figure 4 shows the percentage recovered capacity (C in %) as a function of the number of cycles (N). Curve 9 is the curve obtained with a battery according to the invention as shown schematically in figure 1. During these tests, the technique of operating the battery 10
15 was the same as in the preceding example.

Despite a high discharge rate, it was found that the battery according to the invention using a PEO layer (the PEO being completely gelled after contacting with the liquid electrolyte) between the lithium and the PVDF/HFP-based separator is capable of recovering more than 80% of its initial capacity after 350 cycles.

25 Example 3: Battery constructed from a PVDF membrane coated with a PEO solution

In the previous two examples, the PEO was prepared in the form of a layer before being brought into contact with the liquid electrolyte. In the present example, so 30 as advantageously to eliminate one step in the manufacturing process, the PEO was used directly in gel form. To do this, a solvent (typically acetonitrile) was added to the PEO in order to obtain a gel. Such a battery is shown schematically in figure 5. A thin 35 layer of this solution was spread, using a brush, over the surface of the lithium. Parallel, the cathode/PVDF-HFP separator assembly was impregnated with liquid electrolyte. All this was assembled to form a battery. Thus, the PEO was used directly in gel form.

Example 4: Battery constructed from a PVDF membrane impregnated with a liquid electrolyte in which PEO has been dissolved

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The same principle, explained in Example 3, may be transposed using the liquid electrolyte EC/PC/LiTFSI (1 mol/l) as solvent for the PEO. In this case, the cathode/PVDF-HFP separator complex was imbibed with the 10 gel. The battery cycling conditions shown were the same as in Example 2. The battery tested is shown schematically in figure 5.

15 The capacity retention is identical to that obtained in batteries using a PEO layer.

Figure 6 shows the percentage recovered capacity (C in %) with respect to the number N of cycles for a battery 12 as shown in figure 5. Curve 18 is the curve obtained 20 with such a battery 12 according to the invention.

It may be seen that the capacity retention is identical to that obtained in the batteries according to the invention using a PEO layer.